

Optimized preparation conditions of yttria doped zirconia coatings on potassium ferrate (VI) electrode for alkaline super-iron battery

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HIGHLIGHTS

- ▶ Y_2O_3 – ZrO_2 coatings on K_2FeO_4 electrodes are prepared.
- ▶ Super-iron coin cells are assembled using Y_2O_3 – ZrO_2 coated K_2FeO_4 electrode.
- ▶ The discharge property of super-iron coin cell is superior to Zn/MnO_2 coin cell.
- ▶ Super-iron battery can substitute for present primary batteries in application.
- ▶ Alkaline super-iron battery is expected to become a novel energy resource system.

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ABSTRACT

To enhance the stability of potassium ferrate (VI) (K_2FeO_4) electrodes and their discharge capabilities in alkaline battery systems, yttria (Y_2O_3) doped zirconia (ZrO_2) (denoted as Y_2O_3 – ZrO_2) coatings are utilized to protect the K_2FeO_4 electrode in alkaline electrolytes. The preparation conditions of Y_2O_3 – ZrO_2 coatings on K_2FeO_4 electrodes are investigated in detail and the optimum preparation conditions are determined. Results of discharge tests with open module batteries show that the Y_2O_3 – ZrO_2 coated K_2FeO_4 electrode (prepared under the optimum conditions) provides a superior discharge specific capacity than uncoated and ZrO_2 coated K_2FeO_4 electrodes. Alternatively, to further explore the practical application of K_2FeO_4 electrodes, super-iron coin cells are assembled using a Y_2O_3 – ZrO_2 coated K_2FeO_4 electrode as the cathode and zinc foil as the anode. The discharge specific capacity and discharge specific energy of the coin cell with Y_2O_3 – ZrO_2 coated K_2FeO_4 cathode are $169.8 \text{ mA h g}^{-1}$ and $201.9 \text{ W h kg}^{-1}$ respectively, which are superior to the MnO_2 coin cell. Therefore, the results indicate that Y_2O_3 – ZrO_2 coated K_2FeO_4 cathode is suitable for practical applications in alkaline battery systems. Consequently, the alkaline super-iron battery is expected to become a novel energy resource system that replaces present primary batteries in various electronic devices.

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1. Introduction

At present, our world is facing the progressive depletion of energy resources especially non-renewable fuels and severe environmental concern due to the consumption of fossil fuels for energy is being increased [1–5]. Therefore, it is indispensable for us to develop sustainable, environmentally benign and cost effective energy sources to meet future energy requirements. Energy based on electricity generated from electrochemical batteries is one of the most efficient, convenient and reliable power sources [6,7]

and is used in many fields including portable electronic consumer devices, medical implants, transportation, etc. [8,9]. Among all the electrochemical batteries under research, the alkaline super-iron battery has attracted great interest and been extensively studied in the recent two decades owing to its following attractive advantages [10–15], firstly, alkaline super-iron batteries possess high energy storage capacity (intrinsic three electron capacity) compared to traditional primary batteries which are made of heavy metal oxides with single or less than one electron redox chemistry; secondly, the alkaline super-iron battery has been known as a “green environmental-protective battery” owing to its non-toxic and colloidal Fe (III) discharge products; thirdly, the alkaline super-iron battery is a sustainable energy system for the discharge product (Fe_2O_3) can be recycled and become the raw material of the

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super-iron battery. Therefore, to enhance energy storage density, mitigate environmental pollutants, and improve the sustainability of electrode material utilization of primary batteries, the alkaline super-iron battery is expected to become a novel energy resource and a substitute for present primary batteries in various electronic devices such as mobile electronics, and electric appliance.

Generally, the electrode material of super-iron battery is ferrate (VI), such as K_2FeO_4 , $BaFeO_4$, $CuFeO_4$, and $SrFeO_4$ electrodes [16,17]. Among these Fe (VI) electrodes, K_2FeO_4 electrodes have been paid the most emphasis due to their higher solid-state stability (decomposition/each year is less than 0.1%) and high theoretical special capacity (406 mA h g^{-1}) [10,18]. However, commercial applications of alkaline super-iron batteries based on K_2FeO_4 electrodes have not been implemented due to their chemical instability and self-discharge [19]. Especially, in alkaline battery systems, the formation of Fe (III) overlayer during storage is likely to deteriorate the charge transfer of K_2FeO_4 electrodes. Meanwhile, the resulting Fe (III) overlayer will accelerate the decomposition of K_2FeO_4 electrodes [20,21]. Hence, solving these existing disadvantages is a key step for bringing K_2FeO_4 electrodes into practical application.

To improve the stability of the super-iron battery, ferrate electrodes coated by inorganic materials such as SiO_2 and organic materials such as 2,3-Naphthalocyanine ($C_{48}H_{26}N_8$) have been reported in the previous studies [19,20,22]. Licht et al have repeatedly investigated ceramic material of zirconia (ZrO_2) used as protective coatings to stabilize the K_2FeO_4 electrode [18,21,23], and their investigation results indicate that the ZrO_2 coating significantly stabilizes the high energy K_2FeO_4 electrode, and improves the energy storage capacity of super-iron batteries. For further improving the charge transfer of ZrO_2 coated K_2FeO_4 electrode, in our recent studies, Y_2O_3 – ZrO_2 coatings were utilized to protect the K_2FeO_4 electrode in an alkaline battery system [24], and the result demonstrates that the stability and charge transfer of Y_2O_3 – ZrO_2 coated K_2FeO_4 electrode are superior to that of ZrO_2 coated K_2FeO_4 electrodes. However, up till now, the K_2FeO_4 electrodes have rarely been assembled into real batteries (including coin cells, cylindrical cells, etc.) for systematical investigation in the previous reports, although exploring the discharge performances of real batteries is very important for developing practical applications of alkaline super-iron batteries.

Based on our previous work, super-iron coin cells are assembled using a Y_2O_3 – ZrO_2 coated K_2FeO_4 electrode as the cathode and zinc foil as the anode. To obtain the optimal discharge performance of Y_2O_3 – ZrO_2 coated K_2FeO_4 cathodes, the preparation conditions of Y_2O_3 – ZrO_2 coatings on K_2FeO_4 electrodes were first investigated and determined by open module batteries, and then the application effects of coin cells were evaluated and observed.

2. Material and methods

2.1. Materials

K_2FeO_4 ($\geq 60\%$) was purchased from Wuhan Galaxy Chemical Co. Ltd., and then recrystallized in an ice-bath before utilization ($\geq 97\%$). Zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) and yttrium nitrate ($Y(NO_3)_3 \cdot 6H_2O$) ($\geq 99\%$, Tianjin Bodi Chemical Holding Co. Ltd.), ammoniacal water ($NH_3 \cdot H_2O$) (AR grade, Kewei Corp. of Tianjin University), N-methyl pyrrolidone (NMP) and absolute ether (AR grade, Tianjin Chemical Reagent No. 1 Plant), acetylene black ($\geq 99\%$, Tianjin Jinqiushi Chemical Co. Ltd.), and poly(vinylidene fluoride) (PVdF) ($\geq 99\%$, Chenguang Research Institute of Chemical Industry), MnO_2 (AR grade, Changzhou Xinzhou Chemical Co. Ltd.) were purchased and used as-received. Typical coin cell package (CR2032) was used to assemble all coin cells.

2.2. Preparation of Y_2O_3 – ZrO_2 coated K_2FeO_4 electrodes

Details of the materials synthesis and electrode preparation were described in our previous publication [24]. Specific details are as follows: two drops of deionized water were dispersed in 20 mL ether by ultrasonic dispersion before $ZrOCl_2 \cdot 6H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ were added to the ether, and then stirred with 2.00 g recrystallized K_2FeO_4 in the air for 0.5 h, the solution pH was adjusted with $NH_3 \cdot H_2O$ during the above process, and the precipitation was dried by vertex suction at a set temperature overnight. Finally, K_2FeO_4 with a Y_2O_3 – ZrO_2 coating was obtained. The preparation of cathodes was completed through spreading a measured amount of slurry including the active mass mixed (coated or uncoated K_2FeO_4 powder) with acetylene black (conductive matrix), PVdF (binder), and NMP (solvent) on clean nickel foam. The mass ratio of K_2FeO_4 powder, acetylene black and PVdF is 80:15:5. Next, the as-prepared K_2FeO_4 cathodes were pressed and dried at 333 K for several hours. The net weight of K_2FeO_4 (including acetylene black and PVdF) on the electrode was about 0.25 g.

2.3. Fabrication of Open module battery and super-iron coin cell

The optimum preparation conditions of Y_2O_3 – ZrO_2 coated K_2FeO_4 electrodes were determined by open module batteries, the batteries consisted of coated or uncoated K_2FeO_4 positive electrodes, non-woven polypropylene grafted separator and a zinc (Zn) foil anode, 10 mol L^{-1} KOH served as the electrolyte. In the process of fabricating coin cells, the separator and anode were the same as an open module battery, Y_2O_3 – ZrO_2 coated K_2FeO_4 electrode as cathode materials and electrolyte was the mixture of 10 mol L^{-1} KOH and carboxymethyl cellulose sodium. The coin cell packaging (CR2032) was used to assemble the super-iron coin cell. Stainless steel spacers in the packaging were used as current collectors. A disk of carbon fiber sheet (Spectracarb 2250) was placed between each stainless steel current collector in order to decrease the contact resistance (R_c). The electrolyte was introduced to each electrode and sealed in the coin cell using a coin cell crimper by pressing at 1500 psi. The preparation of a MnO_2 coin cell was similar to the K_2FeO_4 coin cell.

2.4. Electrochemical properties measurement

Electrochemical properties of as-assembled open module batteries and coin cells were studied at 298 K via a Land Battery Test System (CT2001A, Wuhan Jinnuo Electronic Ltd., China). The cut-off voltage was 0.9 V at the discharge current density of 1 mA cm^{-2} .

3. Results and discussion

3.1. Effect of coating amount of Y_2O_3 – ZrO_2 on the discharge performance of K_2FeO_4 cathodes

In this work, it has been found that there are four preparation parameters jointly determining the discharge performance of K_2FeO_4 cathodes, namely, the coating amount of Y_2O_3 – ZrO_2 , the doping amount of Y_2O_3 in Y_2O_3 – ZrO_2 , the pH of the solution for preparing Y_2O_3 – ZrO_2 coated K_2FeO_4 and the temperature for drying Y_2O_3 – ZrO_2 coated K_2FeO_4 .

In order to determine the optimum coating amount of Y_2O_3 – ZrO_2 , the effect of Y_2O_3 – ZrO_2 coating with different quantities on the discharge specific capacity of Y_2O_3 – ZrO_2 coated K_2FeO_4 cathodes was investigated, and four different Y_2O_3 – ZrO_2 coated K_2FeO_4 cathodes were prepared by adjusting the mass ratio of

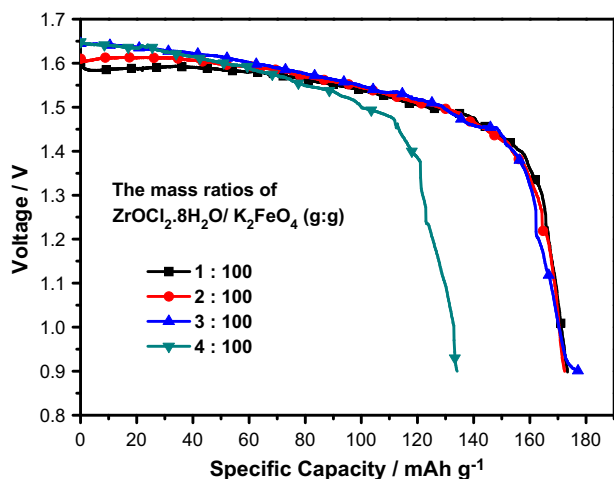


Fig. 1. Effect of coating amount of ZrO_2 on the discharge specific capacity of Y_2O_3 - ZrO_2 coated K_2FeO_4 cathodes in 10 mol L^{-1} KOH electrolyte solution.

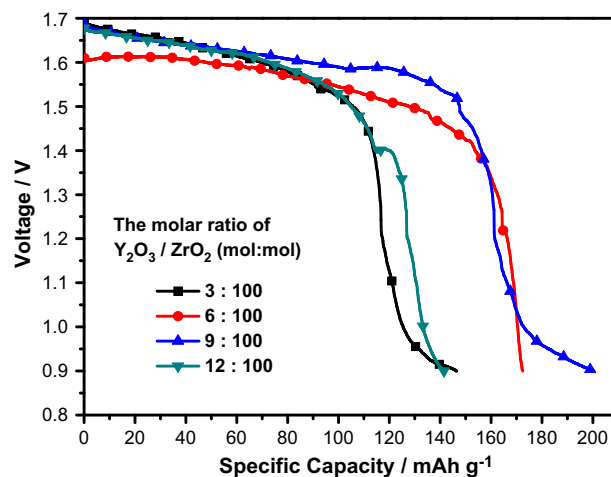


Fig. 2. Effect of coating amount of Y_2O_3 on the discharge specific capacity of Y_2O_3 - ZrO_2 coated K_2FeO_4 cathodes in 10 mol L^{-1} KOH electrolyte solution.

$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{K}_2\text{FeO}_4$ (g:g) and the molar ratio of $\text{Y}_2\text{O}_3/\text{ZrO}_2$ (mol:mol). Specifically, the mass ratios of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{K}_2\text{FeO}_4$ (g:g) are 1:100, 2:100, 3:100 and 4:100 respectively, at the molar ratio of $\text{Y}_2\text{O}_3/\text{ZrO}_2$ (mol:mol) fixed to 6:100 in this investigation. The discharge profiles of as-prepared Y_2O_3 - ZrO_2 coated K_2FeO_4 cathodes at current density of 1 mA cm^{-2} are displayed in Fig. 1. It can be observed from Fig. 1 that when the mass ratio of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{K}_2\text{FeO}_4$ (g:g) is less than 3:100, the discharge specific capacity of the Y_2O_3 - ZrO_2 coated K_2FeO_4 cathodes shows a similar discharge tendency, namely, their discharge specific capacity are basically equal. This result suggests that a small amount of ZrO_2 coating can enhance the discharge performance of K_2FeO_4 cathodes obviously. However, when the mass ratio of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{K}_2\text{FeO}_4$ (g:g) is more than 4:100, the discharge specific capacity of K_2FeO_4 cathodes indeed declines. Reason for this result is as follows: adding excessive zirconium salt can form a large number of zirconium salt colloids, which will increase the thickness of ZrO_2 coatings on the surface of the K_2FeO_4 cathode. Also, too thick films can become a barrier for the transfer of electrons and ions in the electrolyte to the K_2FeO_4 cathode, causing the decline of the conductivity and discharge efficiency of K_2FeO_4 cathode. Meanwhile, excessive zirconium salt will result in forming many new ZrO_2 phases that accumulate among K_2FeO_4 particles, which leads to increasing the resistance of electronic conduction, therefore, the discharge performance of the K_2FeO_4 cathode decreases. Comparing the discharge specific capacity curves of K_2FeO_4 cathodes in Fig. 1, to obtain the optimal discharge performance, the mass ratio of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{K}_2\text{FeO}_4$ (g:g) is confirmed between 2:100 and 3:100. In our work, 2.5:100 was chosen as the mass ratio of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{K}_2\text{FeO}_4$ (g:g) for the following research.

3.2. Effect of doping amount of Y_2O_3 in Y_2O_3 - ZrO_2 coatings on the discharge performance of K_2FeO_4 cathodes

The discharge performance of different Y_2O_3 - ZrO_2 coated K_2FeO_4 cathodes was investigated for confirming the optimum doping amount of Y_2O_3 in Y_2O_3 - ZrO_2 coatings. In this study, the molar ratios of $\text{Y}_2\text{O}_3/\text{ZrO}_2$ (mol:mol) are 3:100, 6:100, 9:100 and 10:100 (denoted as MR-3, MR-6, MR-9, MR-10 respectively) at the mass ratios of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{K}_2\text{FeO}_4$ (g:g) fixed to 2.5:100. The discharge curves of K_2FeO_4 cathodes coated with Y_2O_3 - ZrO_2 at a current density of 1 mA cm^{-2} are exhibited in Fig. 2. It can be seen that when the voltage is cut off at 0.9 V, the discharge specific

capacities of MR-3, MR-6, MR-9, MR-10 coated K_2FeO_4 cathodes are $146.4 \text{ mA h g}^{-1}$, $172.3 \text{ mA h g}^{-1}$, $200.4 \text{ mA h g}^{-1}$ and $141.6 \text{ mA h g}^{-1}$, respectively. These results indicate that the discharge performance of MR-6 and MR-9 coated K_2FeO_4 cathodes presents a better result compared to that of MR-3 and MR-10 coated K_2FeO_4 cathodes. According to the explanation provided by the previous report [24]: when the doping amount of Y_2O_3 in Y_2O_3 - ZrO_2 coatings is too small, the affluent cubic ZrO_2 which can sufficiently enhance the conductivity of ZrO_2 will not be achieved and thus the advantage of Y_2O_3 does not be fully realized; on the other hand, too much Y_2O_3 in ZrO_2 coatings may cause the conductivity of Y_2O_3 - ZrO_2 coatings to decline, as there are fewer oxygen vacancies contributing to conduction. Taking all factors into consideration, when the molar ratio of Y_2O_3 and ZrO_2 (mol:mol) is between 6:100 and 9:100, Y_2O_3 - ZrO_2 coated K_2FeO_4 cathode attains the optimal discharge performance. In our work, the molar ratio of Y_2O_3 and ZrO_2 (mol:mol) was controlled at 9:100 for the subsequent research.

3.3. Effect of solution pH on the discharge performance of Y_2O_3 - ZrO_2 coated K_2FeO_4 cathodes

To determine the optimum pH of solution for preparing Y_2O_3 - ZrO_2 coatings, the solution pH of 4.0, 7.0 and 10.0 were chosen in this study and experimental results are demonstrated in Fig. 3. As seen in Fig. 3, when the discharge voltage reaches 0.9 V, the discharge specific capacity of Y_2O_3 - ZrO_2 coated K_2FeO_4 cathode is 133 mA h g^{-1} under the pH of solution adjusted to 7. However, when the pH of solution is 4 or 10, the discharge specific capacities of Y_2O_3 - ZrO_2 coated K_2FeO_4 cathodes drop markedly. The phenomenon can be analyzed and explained using the effect of pH on the surface electric properties of Y_2O_3 - ZrO_2 colloids. In the process of coating K_2FeO_4 cathodes, when the solution pH is low, the Y_2O_3 - ZrO_2 colloid is difficult to form. Consequently, there is not enough Y_2O_3 - ZrO_2 coating to protect K_2FeO_4 cathode; in contrast, when the solution pH is high, the formation of Y_2O_3 - ZrO_2 colloid is too fast, resulting in Y_2O_3 - ZrO_2 colloid unevenly distributed on the surface of the K_2FeO_4 cathode. Hence, neither case mentioned above can be beneficial for Y_2O_3 - ZrO_2 coatings well distributed on K_2FeO_4 cathodes. Therefore, the suitable pH of solution is between 7 and 8. In this work, we chose 7 as the solution pH for the following research.

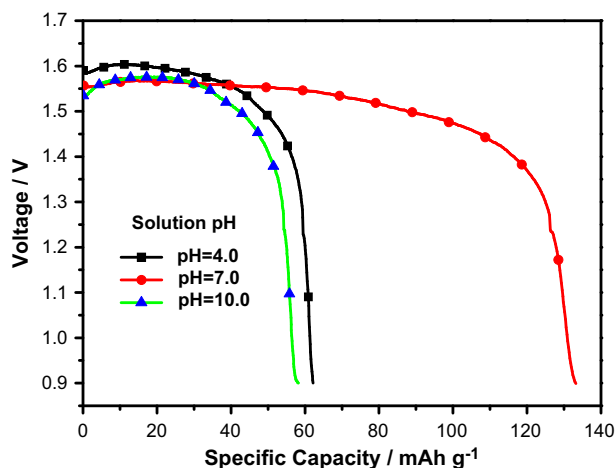


Fig. 3. Effect of solution pH on the discharge specific capacity of Y₂O₃-ZrO₂ coated K₂FeO₄ cathodes in the coating process.

3.4. Effect of drying temperature on the discharge performance of Y₂O₃-ZrO₂ coated K₂FeO₄ cathodes

For investigating the effect of drying temperature on the discharge performance of the Y₂O₃-ZrO₂ coated K₂FeO₄ cathode, the drying temperature of 303 K, 333 K and 363 K were chosen in this investigation and corresponding results are shown in Fig. 4. When the discharge voltage reaches 0.9 V, the discharge specific capacities of Y₂O₃-ZrO₂ coated K₂FeO₄ cathodes are 97.1 mA h g⁻¹ and 135 mA h g⁻¹ under the drying temperature of 303 K and 333 K, respectively. Surprisingly, the discharge specific capacity of Y₂O₃-ZrO₂ coated K₂FeO₄ cathode declines to 84.2 mA h g⁻¹ when drying temperature rises to 363 K (as seen in Fig. 4). That is to say, within a certain temperature range, the discharge performance can be improved by raising the drying temperature; however, increasing the drying temperature continuously will make the discharge specific capacity of Y₂O₃-ZrO₂ coated K₂FeO₄ cathodes decrease abruptly. The reason is that Y₂O₃-ZrO₂ coated K₂FeO₄ cathodes can be rapidly decomposed when temperature surpasses 353 K. Therefore, a drying temperature less than 353 K should be reasonable in this work. Through observing the discharge performance of Y₂O₃-ZrO₂ coated K₂FeO₄ cathodes, the drying temperature fixed

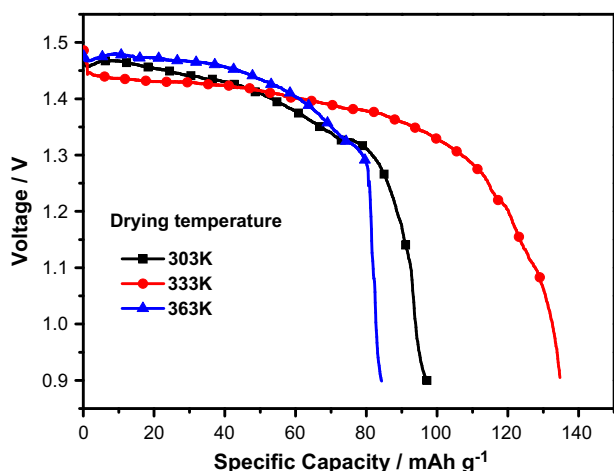


Fig. 4. Effect of drying temperature on the discharge specific capacity of Y₂O₃-ZrO₂ coated K₂FeO₄ cathodes.

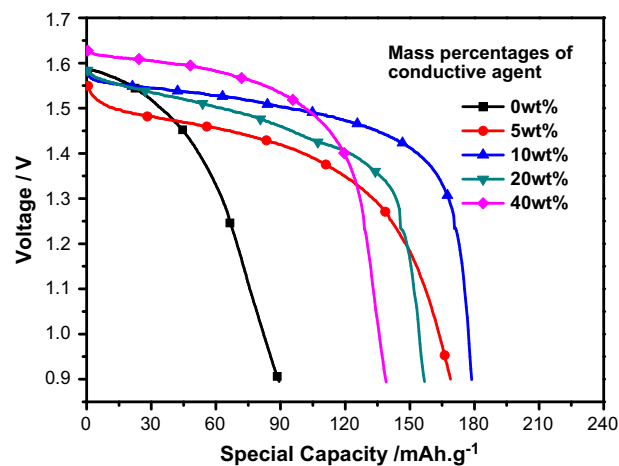


Fig. 5. Discharge curves of Y₂O₃-ZrO₂ coated K₂FeO₄ cathodes with different amounts of conductive agent.

to between 323 and 343 K is appropriate. In our work, 333 K was chosen as a fitting drying temperature for the following research.

3.5. Effect of conductive agent on the discharge performance of Y₂O₃-ZrO₂ coated K₂FeO₄ cathodes

The effect of conductive agent for preparing Y₂O₃-ZrO₂ coated K₂FeO₄ cathodes on the discharge capability of Y₂O₃-ZrO₂ coated K₂FeO₄ cathodes was investigated. In this investigation, the mass percentages of conductive agent (acetylene black) in the Y₂O₃-ZrO₂ coated K₂FeO₄ cathodes were 0%, 5%, 10%, 20% and 40% (denoted as 0 wt.%, 5 wt.%, 10 wt.%, 20 wt.% and 40 wt.%), respectively. It can be observed from Fig. 5, when no conductive agent was added into cathode (0 wt.%), the discharge specific capacity of Y₂O₃-ZrO₂ coated K₂FeO₄ cathode is only 88.9 mA h g⁻¹, and the discharge voltage reduces quickly during the discharge process for serious positive polarization. Obviously, appropriately increasing the content of conductive agent can remarkably improve the discharge specific capacity of Y₂O₃-ZrO₂ coated K₂FeO₄ cathodes. The conductive agent facilitates the charge transfer among the K₂FeO₄ particles and decreases the resistance of Y₂O₃-ZrO₂ coated K₂FeO₄ cathodes. On the other hand, the conductive agent ensures sufficient electrolyte to be used in the cathode and delays the positive polarization. However, too much conductive agent can gradually drop down the discharge specific capacity of Y₂O₃-ZrO₂ coated K₂FeO₄ cathode (as shown in Fig. 5). Increasing content of conductive agent thickens the as-prepared cathodes significantly, hindering the contact between active mass (K₂FeO₄) and electrolyte, meanwhile it also increases the cathode polarization. Therefore both effects negatively influence the discharge performance of the Y₂O₃-ZrO₂ coated K₂FeO₄ cathode. In this work, the appropriate content of conductive agent for preparing Y₂O₃-ZrO₂ coated K₂FeO₄ cathodes ranged between 10% and 15%.

3.6. Discharge performance analysis of Y₂O₃-ZrO₂ coated K₂FeO₄ cathodes in open module battery

In order to validate the effect of Y₂O₃-ZrO₂ coatings on K₂FeO₄ cathodes (prepared under the optimum conditions), uncoated and ZrO₂ coated K₂FeO₄ cathodes were also prepared for comparison purpose. The discharge specific capacities curves of ZrO₂ coated and uncoated K₂FeO₄ cathodes as well as Y₂O₃-ZrO₂ coated K₂FeO₄ cathodes are comparatively presented in Fig. 6. It can be observed from Fig. 6 that when the discharge voltage reaches 0.9 V, the discharge specific capacities of ZrO₂ and Y₂O₃-ZrO₂

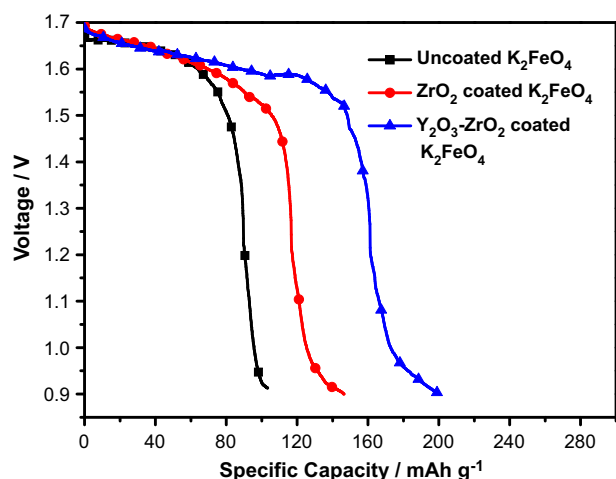


Fig. 6. The discharge performance curves of uncoated K_2FeO_4 cathode and coated K_2FeO_4 cathodes in open module batteries.

coated K_2FeO_4 cathodes are $146.5 \text{ mA h g}^{-1}$ and $200.4 \text{ mA h g}^{-1}$ respectively, in contrast to the specific capacity of $103.4 \text{ mA h g}^{-1}$ from the uncoated K_2FeO_4 cathode. Apparently, the discharge specific capacity of the $Y_2O_3-ZrO_2$ coated K_2FeO_4 cathode is much higher than that of the uncoated K_2FeO_4 cathode. Alternatively, it should be noted that the discharge specific capacity of ZrO_2 coated K_2FeO_4 cathode is not remarkably improved compared with that of the uncoated K_2FeO_4 cathode. The reason is that although ZrO_2 coatings can stabilize K_2FeO_4 cathode in alkaline electrolyte by preventing K_2FeO_4 cathode from forming Fe (III) overlayers which can accelerate the decomposition of K_2FeO_4 electrodes, the conductive property of pure ZrO_2 is very poor, resulting that pure ZrO_2 coating becomes a barrier for ions exchange and charge transfer in alkaline electrolyte. It is generally recognized that the addition of $Y_2O_3-ZrO_2$ can improve the conductivity of ZrO_2 coatings [24]. Therefore, the employment of $Y_2O_3-ZrO_2$ coatings layer not only can protect K_2FeO_4 cathode from forming Fe (III) overlayers, but also can facilitate the ions transportation and charge transfer in alkaline electrolyte. Consequently, the specific capacity of $Y_2O_3-ZrO_2$ coated K_2FeO_4 cathode is obviously enhanced (see Fig. 6).

3.7. Effect of temperature on the discharge performance of K_2FeO_4 coin cell

To examine the applicability of $Y_2O_3-ZrO_2$ coated K_2FeO_4 electrodes under practical work conditions, $Y_2O_3-ZrO_2$ coated K_2FeO_4 electrodes were assembled into coin cells (denoted as Zn/YZ- K_2FeO_4 coin cell). Fig. 7 is the digital image of an as-prepared super-iron coin cell. The effect of temperature on the discharge performance of Zn/YZ- K_2FeO_4 coin cell was investigated. Fig. 8 shows the discharge curves of Zn/YZ- K_2FeO_4 coin cells at 293 K, 313 K and 333 K. As seen in Fig. 8, the discharge curve of Zn/YZ- K_2FeO_4 coin cell at 293 K is smooth and stable. However, when the surrounding temperature is 313 K or 333 K, the discharge curves of Zn/YZ- K_2FeO_4 coin cells fluctuate severely; besides, the voltage linearly declines when discharged for a certain time. The phenomenon is partly caused by external factors, specifically, the experimental temperature fluctuations and changes around the set temperature, resulting in the discharge voltage of Zn/YZ- K_2FeO_4 coin cell is unstable during the discharge process. More importantly, the active mass (K_2FeO_4) of cathode in Zn/YZ- K_2FeO_4 coin cell easily decomposes under high temperature, leading to the discharge voltage appear a sudden drop during the



Fig. 7. Digital image of Zn/YZ- K_2FeO_4 coin cells.

discharge process. Therefore, the reasonable work temperature for Zn/YZ- K_2FeO_4 coin cell should be below 313 K.

3.8. Analysis of discharge performance of coin cells

To compare the discharge performance of Zn/YZ- K_2FeO_4 coin cell with a conventional Zn/ MnO_2 battery, MnO_2 electrode material was also assembled into a coin cell (denoted as Zn/ MnO_2 coin cell). Fig. 9 exhibits the discharge curves of Zn/YZ- K_2FeO_4 coin cell and Zn/ MnO_2 coin cell. As shown in Fig. 9, when the discharge voltage is cut off to 0.9 V, the discharge specific capacity and specific energy of Zn/YZ- K_2FeO_4 coin cell are $169.8 \text{ mA h g}^{-1}$ and $201.9 \text{ W h kg}^{-1}$ respectively, obviously higher than that of Zn/ MnO_2 coin cell. In addition, the discharge voltage plateau of Zn/YZ- K_2FeO_4 coin cell is more stable than that of Zn/ MnO_2 coin cell, and the discharge voltage of the Zn/YZ- K_2FeO_4 coin cell is about 0.25 V higher than that of Zn/ MnO_2 coin cell. Therefore, it can be concluded that the Zn/YZ- K_2FeO_4 coin cell is superior to the Zn/ MnO_2 coin cell in terms of discharge performance. Moreover, K_2FeO_4 cathode is more environmental-friendly than the MnO_2 cathode and the raw material of K_2FeO_4 cathode is more abundant than that of the MnO_2 cathode.

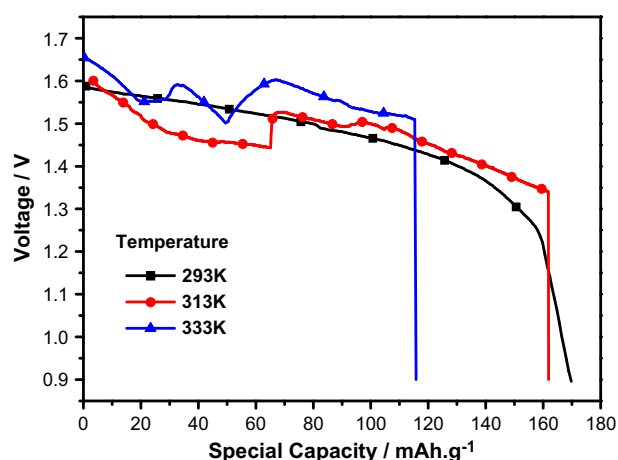


Fig. 8. Effect of work temperature on the discharge specific capacity of Zn/YZ- K_2FeO_4 coin cells.

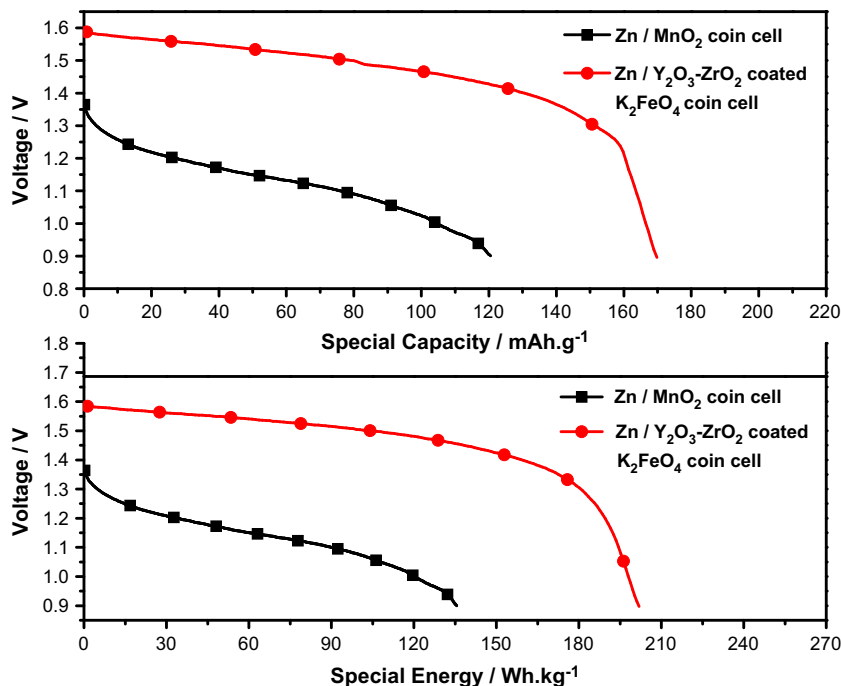


Fig. 9. The discharge performance curves of $\text{Y}_2\text{O}_3\text{-ZrO}_2$ coated K_2FeO_4 coin cells and Zn/MnO_2 coin cell.

4. Conclusions

The paper presents a novel method utilizing Y_2O_3 doped ZrO_2 as a protecting coating to improve the stability and charge transfer of K_2FeO_4 electrode in alkaline electrolytes. Preparation conditions of $\text{Y}_2\text{O}_3\text{-ZrO}_2$ coating on K_2FeO_4 electrode have been investigated, with the optimum coating conditions identified as below: the mass ratio of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{K}_2\text{FeO}_4$ (g:g) from between 2:100 and 3:100, the molar ratio of $\text{Y}_2\text{O}_3/\text{ZrO}_2$ (mol:mol) from between 6:100 and 9:100, the coating pH is adjusted to be 7 or 8, the drying temperature of 333 K and 10–15% content of conductive agent for preparing $\text{Y}_2\text{O}_3\text{-ZrO}_2$ coated K_2FeO_4 electrode. The discharge tests with an open module battery show that the discharge specific capacity of a $\text{Y}_2\text{O}_3\text{-ZrO}_2$ coated K_2FeO_4 electrode (prepared under optimum preparation conditions) is obviously higher than that of an uncoated K_2FeO_4 electrode. Alternatively, a super-iron coin cell is assembled using a $\text{Y}_2\text{O}_3\text{-ZrO}_2$ coated K_2FeO_4 electrode as cathode and zinc foil as the anode. The coin cell with a $\text{Y}_2\text{O}_3\text{-ZrO}_2$ coated K_2FeO_4 cathode exhibits a discharge specific capacity of 169.8 mAh g^{-1} and discharge specific energy of 201.9 Wh kg^{-1} , respectively. Discharge result shows that the electrochemical properties of $\text{Zn/YZ-K}_2\text{FeO}_4$ coin cell are superior to that of Zn/MnO_2 coin cell. Therefore, with a view point for enhancing energy storage density; mitigating environmental pollutants, and improving the sustainability of electrode material utilization of primary batteries; the alkaline super-iron battery is expected to become a novel energy resource and is likely to replace the present primary batteries in various electronic devices.

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